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(54) METHOD AND APPARATUS FOR POWER GENERATION WITH DIMETHYL ETHER MODIFICATION GAS

(57)Abstract:

PROBLEM TO BE SOLVED: To generate power at a high efficiency by using, as a motor fuel, a hydrogen gas or a synthetic gas obtd. by the catalytic modification of dimethyl ether with steam or a carbon dixide gas.

SOLUTION: Examples of a catalyst used for the modification reaction of dimethyl ether are copper catalysts [e.g. metal copper, copper (I) oxide, or copper (II) oxide], iron catalysts [e.g. metal iron, iron (II) oxide, or iron (III) oxide], cobalt catalysts [e.g. metal cobalt, cobalt (II) oxide, or cobalt (III) oxide], and palladium catalysts each comprising palladium carried by a metal, oxide having a basic group. Based on 1 mol of dimethyl ether, 1-20 mol, pref. 1-10 mol, of steam or 0.8-2.0 mol, pref. 0.9-1.5 mol, of carbon dioxide is used; and when both steam and carbon dioxide are used, their total amt. is 1-10 mol, pref. 1-5 mol. The reaction is conducted pref. at 250-450°C under a pressure of from normal pressure to 10 kg/cm2.

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* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention reforms wood ether, obtains synthesis gas or hydrogen gas, and relates to the approach and equipment which use this gas as a fuel for prime movers, and generate it.
[0002]
[Description of the Prior Art] Conventionally, some approaches of generating using wood ether are learned.
[0003] For example, wood ether and a methanol are produced jointly and stored in JP,2-9833,A and JP,3-52835,A from synthesis gas, and the generation-of-electrical-energy approach which uses this for the peak period of a natural gas generation of electrical energy in a comprehensive gasification combined cycle power plant is indicated.
[0004] The generation-of-electrical-energy approach which uses methanol reformed gas on the other hand is well-known. This approach is an approach of obtaining the synthesis gas or hydrogen gas used as a fuel for a generation of electrical energy by refining of a methanol, or decomposition.
[0005] In the methanol-reforming generating-electricity method, the approach of carrying out a carburation to refining or the decomposition reaction which is endothermic reaction using exhaust air and the combustion gas of the turbine for a generation of electrical energy is also proposed. For example, the heat recovery approach of using the heating value of the combustion gas of the thermal heating furnace for heat supply required for progress of a reaction and evaporation heating of material gas for heating of a raw material in the methanolysis equipment which manufactures synthesis gas from a methanol and water is indicated by JP,62-132701,A.
[0006]
[Problem(s) to be Solved by the Invention] However, in the generation-of-electrical-energy approach indicated by JP,2-9833,A and JP,3-52835,A, the publication about the concrete generation-of-electrical-energy approach is absolutely none.
[0007] Moreover, although the effectiveness of a generation of electrical energy will improve by the methanol-reforming generating-electricity method by carrying out a carburation to refining of a raw material methanol, or decomposition using exhaust air and combustion-gas waste heat of the turbine for a generation of electrical energy, a heating value recoverable by the steam-reforming reaction of a methanol and the decomposition reaction of a methanol cannot necessarily say that it is large, as show in (1) and (2) types, respectively.
$CH_3OH+H_2O \rightarrow CO_2+3H_2$ -11.8 kcal/mol (1) $CH_3OH \rightarrow CO+2H_2$ -21.7 kcal/mol (2) [0008] Moreover, since a methanol had toxicity, it had problems, such as requiring the handling caution.
[0009] This invention solves the above-mentioned conventional trouble, and aims at offering the high generation-of-electrical-energy approach of effectiveness.
[0010]
[Means for Solving the Problem] this invention persons came to think out the approach of using this gas as a fuel for prime movers, and generating it wholeheartedly paying attention to the method of reforming wood ether and obtaining synthesis gas or hydrogen gas which this invention persons developed previously as a result of examination that the above-mentioned technical problem should be solved.
[0011] Namely, by adding and carrying out catalytic reaction of a steam or the carbon dioxide gas to wood ether, this invention reforms wood ether and obtains synthesis gas or hydrogen gas. The generation-of-electrical-energy approach which is characterized by using this gas as a fuel for prime movers and which uses wood ether reformed gas, The above-mentioned generation-of-electrical-energy approach characterized by performing refining of wood ether using inside [of 200 to 500 degrees C] low-temperature waste heat, And the refining reactor filled up with the catalyst which makes wood ether, a steam, or carbon dioxide gas react, and makes synthesis gas or hydrogen gas generate, The power

plant which consists of a combustor which burns this synthesis gas or hydrogen gas, and a generator which has the gas turbine rotated with the combustion gas which occurs with this combustor is offered.

[0012] As shown in the following (3) - (5) type, the refining reaction of the wood ether concerning this invention has the large heating value of endothermic reaction, therefore 1.5 to 2.5 times as many exhaust heat recovery as this is possible for it as compared with the refining reaction of the methanol which is the existing technique, and the heating value at the time of combustion of the part and reformed gas also increases it.

$CH_3OCH_3+H_2O \rightarrow 2CO+4H_2$ -48.9 kcal/mol (3) $CH_3OCH_3+3H_2O \rightarrow 2CO_2+6H_2$ -29.3 kcal/mol (4) $CH_3OCH_3+CO_2 \rightarrow 3CO+3H_2$ -58.8 kcal/mol (5) [0013] For example, if steam reforming of the wood ether of 1Nm3 which have 15,580kcal /of gross calorific value of 3 Nm is carried out according to (3) types 2Nm of the carbon monoxide of 3 and the synthesis gas of 6Nm3 which consist of the hydrogen of 3 4Nm are obtained, this synthesis gas gross calorific value is set to 18,240kcal, and the amount of carburations is 2,660kcal. Moreover, the rate of a carburation (value which ** (ed) the amount of carburations with the gross calorific value of wood ether, and doubled it 100) is calculated with 17.1%. On the other hand, at the refining reaction of a methanol, if it decomposes for example, according to (2) types, the methanol steam of 1Nm3 which have 8,150kcal /of gross calorific value of 3 Nm 1Nm of the carbon monoxide of 3 and the synthesis gas of 3Nm3 which consist of the hydrogen of 3 2Nm are obtained, this synthesis gas gross calorific value is set to 9,120kcal, and the amount of carburations is 970kcal. Moreover, the rate of a carburation (value which **(ed) the amount of carburations with the gross calorific value of a methanol steam, and doubled it 100) is calculated with 11.9%.

[0014] Moreover, wood ether is already used as a blowout agent for sprays, and it is checked compared with the methanol that toxicity is very small.

[0015]

[Embodiment of the Invention] This invention consists of generations of electrical energy by refining of wood ether, and the obtained reformed gas.

[0016] The catalyst which wood ether is reformed [catalyst] and makes synthesis gas or hydrogen gas generate has the copper system catalyst which this invention persons developed, an iron system catalyst, a cobalt system catalyst, and a palladium system catalyst.

[0017] A copper system catalyst contains a copper metal and/or a copper compound. As a copper compound, a copper oxide is desirable, and a copper oxide is a cuprous oxide (Cu_2O), a cupric oxide (CuO), or its mixture.

[0018] An iron system catalyst contains an iron metal and/or an iron compound. As an iron compound, an iron oxide is desirable, and an iron oxide is a ferrous oxide (FeO), ferric oxide (Fe_2O_3), or its mixture.

[0019] A cobalt system catalyst contains the metal and/or compound of cobalt. As a compound of cobalt, the oxide of cobalt is desirable, and the oxide of cobalt is the first cobalt (CoO) of oxidization, the second cobalt (Co_2O_3) of oxidization, or its mixture.

[0020] They can be used making catalyst support able to support this copper system catalyst, an iron system catalyst, and a cobalt system catalyst. As desirable catalyst support, although it is oxides, such as an alumina, silica gel, silica alumina, a zeolite, a titania, a zirconia, a zinc oxide, tin oxide, a lanthanum trioxide, and cerium oxide, since the yield of synthesis gas or hydrogen gas is high, an alumina is desirable especially. The content of the copper in a copper system catalyst is 3 - 30 % of the weight preferably about one to 50% of the weight. The content of the iron in an iron system catalyst is 30 - 100 % of the weight preferably about ten to 100% of the weight. Moreover, the content of the cobalt in a cobalt system catalyst is 3 - 15 % of the weight preferably about one to 30% of the weight. The yield of synthesis gas or hydrogen falls that the above [content] is out of range.

[0021] Moreover, other metals or compounds can be combined besides an iron metal and/or a compound, and it can use for the catalyst of this invention. In the case of a copper system catalyst and an iron system catalyst, in the case of zinc, nickel, chromium, manganese, tin, a cerium, lanthanums, these compounds, and a cobalt system catalyst, nickel, iron, and these compounds can be mentioned as other metals and an example of a compound. Especially in the case of an iron system catalyst, in these, the oxide of zinc, nickel, chromium, and manganese is desirable. When the example of a desirable catalyst is given, with a copper system catalyst, there is a cobalt-alumina catalyst by the ferrous-oxide-chromic oxide-alumina catalyst and the cobalt system catalyst in a copper oxide 1 nickel-oxide-zinc oxide-alumina catalyst and an iron system catalyst. Moreover, these metals and compounds are used independently, and also two or more sorts can also be mixed and used. Especially the content of these 3rd component is usually about 1 - 30 % of the weight, when it is 50 or less % of the weight and makes it contain 70 or less % of the weight in the case of a copper system catalyst. When it is 30 or less % of the weight and makes it contain 50 or less % of the weight especially in the case of an iron system catalyst, it is usually about 1 - 20 % of the weight. Moreover, when it is 10 or less % of the weight and makes it contain 20 or less % of the weight especially in the case of a cobalt system catalyst, it is usually

about 1 - 5 % of the weight.
[0022] The general preparation approach of this kind of catalyst is applicable to manufacture of these catalysts. For example, as for the raw material for manufacture of a catalyst, organic-acid salts, such as inorganic-acid salts, such as each nitrate, a carbonate, and a halogenide, and acetate, and an oxalate, are used as copper, iron, or a cobalt compound. Moreover, techniques, such as the usual settling, the kneading method, an impregnation method, and an ion-exchange method, can be used for support actuation of the copper to catalyst support, iron, and cobalt. Thus, if the prepared catalyst constituent has the need, it will be calcinated with a conventional method. As for baking, it is desirable to carry out by heating for 1 to 10 hours at the temperature of 350-800 degrees C into nitrogen or air.
[0023] A palladium system catalyst makes the metallic oxide which has basicity support palladium. The metallic oxides which have basicity are the oxide of the rare earth elements of the oxide of alkaline earth metal, such as an oxide of alkali metal, such as Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O, and BeO, MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, and CeO_2 grade, ZnO, SnO_2 and ZrO_2, aluminum2O3, TiO_2, and two or more sorts of mixture of the aforementioned metallic oxide. Desirable things are a palladium-zinc oxide catalyst, a palladium-sodium oxide-alumina catalyst, etc. Moreover, other metallic oxides which do not have basicity for the metallic oxide which has the aforementioned basicity, for example, silica gel etc., can be used combining other compounds which do not have basicity, for example, silicon carbide, activated carbon, etc. The rate of support of palladium is 0.2 - 20 % of the weight preferably about 0.1 to 30% of the weight to the metallic oxide which has basicity. The yield of synthesis gas falls that the rates of support of palladium are less than about 0.1 % of the weight and 30 % of the weight or more.
[0024] After the manufacture approach of a palladium system catalyst makes the metallic oxide which has basicity support palladium, it is characterized by processing in a basic water solution. As the manufacture approach of this catalyst, the metallic oxide which has basicity is invested in the water solution containing the metal salt of palladium, for example, the water solution containing a palladium chloride, and it calcinates after evaporation to dryness and desiccation. As for baking, it is desirable to carry out by heating for 1 to 10 hours at the temperature of 350-600 degrees C into nitrogen or air. Subsequently, this thing is processed in a basic water solution. As a basic water solution, the water solution of the hydroxide of the hydroxide of alkali metal, a carbonate, and alkaline earth metal is raised. One to about ten are [0.5 to about 20] usually suitable for the concentration of these basic compounds. Processing contacts a basic water solution for a catalyst, and is performed by subsequently removing a basic water solution. It is desirable to perform this processing in ordinary temperature -80 degree C temperature for 1 to 5 hours. Moreover, after processing in a basic water solution, small quantity (0.1 to about [for example,] 1.0) support of the above-mentioned basic compound can also be carried out.
[0025] Although a catalyst performs activation in the culmination of preparation, this is 350-600 degrees C in temperature under a hydrogen ambient atmosphere, and processing for 1 to 10 hours is desirable.
[0026] Thus, by circulating the mixed gas of wood ether, a steam, and/or a carbon dioxide for the prepared catalyst, synthesis gas and/or hydrogen gas are obtained by high yield.
[0027] In this invention, a steam and/or a carbon dioxide are supplied with the wood ether of a raw material. the steam to supply -- the wood ether of a raw material -- receiving -- more than the amount of stoichiometry -- it is -- ****ing -- 1-20-mol twice -- it is 1-10-mol twice preferably. It is not economical if [than 20 mol twice] more [a high wood ether invert ratio will not be obtained if there is less supply of a steam than one mol twice, and]. the carbon dioxide to supply -- the wood ether of a raw material -- receiving -- 0.8-2.0-mol twice -- it is 0.9-1.5-mol twice preferably. If there is less supply of a carbon dioxide than 0.8-mol twice, a high wood ether invert ratio will not be obtained, and when [than 2.0 mol twice] more, a lot of carbon dioxides remain in synthesis gas, and it is necessary to remove a carbon dioxide from synthesis gas, and it is not desirable. moreover -- the case where both a steam and a carbon dioxide are supplied -- the sum total of a steam and a carbon dioxide -- wood ether -- receiving -- 1-10-mol twice -- it is 1-5-mol twice preferably. If [than ten mol twice] more [a high wood ether invert ratio will not be obtained if there is less sum total of a steam and a carbon dioxide than one mol twice, and], it is not economical, and it is not needed [of a carbon dioxide] from synthesis gas, and desirable. Components other than wood ether, a steam, and a carbon dioxide can also be included in this material gas. Inactive gas, for example, nitrogen, inert gas, CO and H2, methane, etc. can be included in a reaction as other components. If below 30 capacity % is suitable for these contents and it increases more than this, lowering of a reaction rate will become a problem. On the other hand, since wood ether burned, if possible, air (oxygen) was eliminated, it is [way] good and an allowance content is 5% or less as air.
[0028] 200-500 degrees C of reaction temperature are 250-450 degrees C preferably. If reaction temperature is lower than 200 degrees C, a high wood ether invert ratio will not be obtained, and if higher than 500 degrees C, generation of the hydrocarbon which makes a subject the methanol, the carbon monoxide, or methane which carries out a byproduction will become remarkable, and neither the synthesis gas in a product nor the rate of hydrogen gas falls and

is desirable.
[0029] In the approach of this invention, it is desirable to give heat of reaction required for the refining reaction of wood ether with the inside [of 200-500 degrees C] low-temperature waste heat generated in an iron mill, an electric power plant, etc. For example, the increment in the calorific value equivalent to the heating value of a refining reaction can be expected to the reformed gas obtained by using the cooler exhaust gas sensible heat generated at the sintering works of an iron mill, or using exhaust air of the gas turbine of an electric power plant. And by performing the refining reaction of wood ether under existence of the above-mentioned catalyst, it goes on at the temperature of 200-500 degrees C, and is suitable for the waste heat of inside low temperature, or recovery of exhaust air.
[0030] Ordinary pressure -10 kg/cm2 of reaction pressure is desirable. If reaction pressure is higher than 10kg/cm2, a wood ether invert ratio will fall.
[0031] 1000-50000m3/m3 and h of space velocity (speeds of supply m3/h of mixed gas [in / 1m of catalysts / the reference condition per three]) are desirable. A reactor becomes extremely large and is not economical if smaller [if space velocity is larger than 50000m3/m3 and h, a wood ether invert ratio will become low, and] than 1000m3/m3 and h.
[0032] In addition, in the approach of this invention, which equipment of the fixed bed and the fluid bed may be used.
[0033] The reformed gas of wood ether is the gaseous fuel which made hydrogen or hydrogen, and a carbon monoxide the subject, and is used as a fuel for prime movers for a generation of electrical energy, such as a gas turbine. The combustion method is possible also for low-temperature combustion, such as others, catalyzed combustion, rarefied gas combustion, etc. of the usual combustion method, and can expect generating control of nitrogen oxides in this case.
[0034] Combustion conditions are the same as that of the conventional approach using LNG or LPG, and are good.
[0035]
[Example]
The water solution which dissolved 91g (Cu(NO3) 2and3H2O) of one to example of catalyst 4 copper nitrates, 73g (Zn (NO3) 2.6H2O) of zinc nitrate, and 368g (aluminum(NO3) 3.9H2O) of aluminium nitrates in about 2l. of ion exchange water, The water solution which dissolved about 250g (Na2CO3) of sodium carbonates in about 2l. of ion exchange water was dropped over about 2 hours into the container made from stainless steel of about 5l. of ion exchange water which kept it warm at about 80 degrees C into which it went, adjusting so that pH may be held 8.0**0.5. It riped by holding as it is for about 1 hour after dropping termination. In addition, when it seemed that pH separated from 8.0**0.5 in the meantime, the nitric-acid water solution of about 1 mol/l or the sodium-carbonate water solution of about 1 mol/l was dropped, and pH was united with 8.0**0.5. Next, it washed using ion exchange water after filtering the generated precipitation until nitrate ion was no longer detected by the penetrant remover. After drying the obtained cake at 120 degrees C for 24 hours, it calcinated at 350 degrees C among air further for 5 hours. Furthermore, this thing was classified in 20-40 meshes, and the target catalyst was acquired.
[0036] The presentation of the acquired catalyst was CuO:ZnO:aluminum2O3=30:20:50 (weight ratio).
[0037] In the approach of the example 5 of a catalyst - the examples 1-4 of 8 catalysts, the catalyst was prepared by the same approach as the examples 1-4 of a catalyst except using 105g (Cr(NO3) 2and3H2O) of chromium nitrates instead of zinc nitrate.
[0038] The presentation of the acquired catalyst was CuO:Cr2O3:aluminum2O3=30:20:50 (weight ratio).
[0039] The coil made from stainless steel with a [reaction approach] bore of 20mm was filled up with the above-mentioned catalyst of the specified quantity. Specified quantity supply was carried out and wood ether and a carbon dioxide were made to react to this coil at predetermined temperature.
[0040] The gas chromatograph analyzed the resultant and unreacted object which were obtained by the above actuation.

[0041] A [reaction condition and experimental result] reaction condition and an experimental result are shown in tables 1 and 2.
[0042]
[Equation 1]

$$\text{合成ガス収率（\%）} = \frac{1/6 \times (\text{CO生成速度} + \text{H}_2\text{生成速度})}{\text{ジメチルエーテル供給速度}} \times 100$$

[0043]
[Equation 2]

$$\text{炭化水素収率（\%）} = \frac{\Sigma[n/2 \times \text{炭化水素（炭素数}n\text{）生成速度}]}{\text{ジメチルエーテル供給速度}} \times 100$$

The units of each rate are all. [mol/g-cat-h] [0044]
[A table 1]

第 1 表

			触媒例 1	触媒例 2	触媒例 3	触媒例 4
触媒 (重量比)			$CuO-ZnO-Al_2O_3$(30 : 20 : 50)			
条件	温度 (℃)		250	300	350	300
	CO_2/ジメチルエーテル (モル比)		1	1	1	2
	空間速度 (h^{-1})		5000	5000	5000	3000
反応成績	ジメチルエーテル転化率 (%)		74.8	78.2	83.1	85.5
	収率 (%)	合成ガス	74.1	76.0	79.8	85.1
		炭化水素	0.7	2.2	3.7	0.4
	合成ガス中 H_2／CO (モル比)		0.98	0.92	0.86	0.72

[0045]
[A table 2]

第 2 表

			触媒例 5	触媒例 6	触媒例 7	触媒例 8
触媒 (重量比)			$CuO-Cr_2O_3-Al_2O_3$(30 : 20 : 50)			
条件	温度 (℃)		250	300	350	300
	CO_2/ジメチルエーテル (モル比)		1	1	1	2
	空間速度 (h^{-1})		5000	5000	5000	3000
反応成績	ジメチルエーテル転化率 (%)		69.3	73.5	77.4	80.7
	収率 (%)	合成ガス	69.0	72.1	75.6	80.6
		炭化水素	0.3	1.4	1.8	0.1
	合成ガス中 H_2／CO (モル比)		0.99	0.95	0.91	0.89

[0046] 91g (Cu(NO3) 2and3H2O) of nine to example of catalyst 11 copper nitrates, 39g (nickel(NO3) 2.6H2O) of nickel nitrate, The water solution which dissolved 37g (Zn(NO3) 2.6H2O) of zinc nitrate, and 368g (aluminum(NO3) 3.9H2O) of aluminium nitrates in about 2l. of ion exchange water, The water solution which dissolved about 200g of sodium hydroxides in about 2l. of ion exchange water was dropped over about 1 hour into the container made from stainless steel of about 5l. of ion exchange water which kept it warm at about 60 degrees C into which it went, adjusting so that pH may be held 8.0**0.5. It riped by holding as it is for about 1 hour after dropping termination. In addition, when it seemed that pH separated from 8.0**0.5 in the meantime, the nitric-acid water solution of about 1 mol/l or the sodium-hydroxide water solution of about 1 mol/l was dropped, and pH was united with 8.0**0.5. Next, it washed using ion exchange water after filtering the generated precipitation until nitrate ion was no longer detected by the penetrant remover. After drying the obtained cake at 120 degrees C for 24 hours, it calcinated at 350 degrees C among air further for 5 hours. Furthermore, this thing was classified in 20-40 meshes, and the target catalyst was acquired.
[0047] The presentation of the acquired catalyst was CuO:NiO:ZnO:aluminum2O3=30:10:10:50 (weight ratio).
[0048] In the approach of the examples 9-11 of example of catalyst 12 catalyst, the catalyst was prepared by the same

approach as the examples 9-11 of a catalyst except using 53g (Cr(NO3) 2and3H2O) of chromium nitrates instead of nickel nitrate.
[0049] The presentation of the acquired catalyst was CuO:Cr2O3:ZnO:aluminum2O3=30:10:10:50 (weight ratio).
[0050] In the approach of the examples 9-11 of example of catalyst 13 catalyst, the catalyst was prepared by the same approach as the examples 9-11 of a catalyst except using 33g (Mn(NO3) 2.6H2O) of manganese nitrate instead of nickel nitrate.
[0051] The presentation of the acquired catalyst was CuO:MnO2:ZnO:aluminum2O3=30:10:10:50 (weight ratio).
[0052] In the approach of the example 13 of example of catalyst 14 catalyst, the catalyst was prepared by the same approach as the examples 9-11 of a catalyst except using 53g (Cr(NO3) 2and3H2O) of chromium nitrates instead of zinc nitrate.
[0053] The presentation of the acquired catalyst is CuO:Cr 2O3. : It was MnO2:aluminum2O3=30:10:10:50 (weight ratio).
[0054] The coil made from stainless steel with a [reaction approach] bore of 20mm was filled up with the above-mentioned catalyst of the specified quantity. Specified quantity supply was carried out and wood ether and a steam were made to react to this coil at predetermined temperature.
[0055] The gas chromatograph analyzed the resultant and unreacted object which were obtained by the above actuation.

[0056] A [reaction condition and experimental result] reaction condition and an experimental result are shown in tables 3 and 4.
[0057]
[Equation 3]

$$\text{水素収率（\%）} = \frac{\frac{1}{6}\times(\text{H}_2\text{生成速度} - 2\times\text{CO生成速度}) + \frac{1}{4}\times\text{CO生成速度}}{\text{ジメチルエーテル供給速度}} \times 100$$

[0058]
[Equation 4]

$$\text{メタノール収率（\%）} = \frac{\frac{1}{2}\times\text{メタノール生成速度}}{\text{ジメチルエーテル供給速度}} \times 100$$

[0059]
[Equation 5]

$$\text{CO収率（\%）} = \frac{\frac{1}{4}\times\text{CO生成速度}}{\text{ジメチルエーテル供給速度}} \times 100$$

The units of each rate are all. [mol/g-cat-h] [0060]
[A table 3]

第 3 表

			触媒例 9	触媒例 10	触媒例 11
触媒（重量比）			$CuO-NiO-ZnO-Al_2O_3$ (30 : 10 : 10 : 50)	$CuO-NiO-ZnO-Al_2O_3$ (30 : 10 : 10 : 50)	$CuO-NiO-ZnO-Al_2O_3$ (30 : 10 : 10 : 50)
条件	温度（℃）		200	250	300
	H_2O/ジメチルエーテル（モル比）		10	10	10
	空間速度（h^{-1}）		15000	15000	15000
反応成績	ジメチルエーテル転化率（%）		83.3	98.1	100
	収率（%）	水素	79.2	92.0	88.5
		メタノール	2.5	3.8	6.2
		炭化水素	0.1	0.1	0.3
		CO	1.5	2.2	4.9

[0061]
[A table 4]

第 4 表

			触媒例12	触媒例13	触媒例14
触媒(重量比)			$CuO-Cr_2O_3-ZnO-Al_2O_3$ (30:10:10:50)	$CuO-MnO_2-ZnO-Al_2O_3$ (30:10:10:50)	$CuO-Cr_2O_3-MnO_2-Al_2O_3$ (30:10:10:50)
条件	温度(℃)		250	250	250
	H_2O/ジメチルエーテル(モル比)		10	10	10
	空間速度(h^{-1})		15000	15000	15000
反応成績	ジメチルエーテル転化率(%)		94.3	92.2	91.8
	収率(%)	水素	86.4	85.1	84.6
		メタノール	4.3	4.1	3.8
		炭化水素	0.1	0.1	0.1
		CO	3.5	2.9	3.3

[0062] 405g (Fe(NO3) 3.9H2O) of 15 to example of catalyst 17 iron nitrate, 79g (Cr(NO3) 2and3H2O) of chromium nitrates, and the water solution which dissolved 37g (aluminum(NO3) 3.9H2O) of aluminium nitrates in about 2l. of ion exchange water, The water solution which dissolved about 180g of sodium hydroxides in about 2l. of ion exchange water was dropped over about 1 hour into the container made from stainless steel of about 5l. of ion exchange water which kept it warm at about 80 degrees C into which it went, adjusting so that pH may be held 8.0**0.5. It riped by holding as it is for about 1 hour after dropping termination. In addition, when it seemed that pH separated from 8.0**0.5 in the meantime, the nitric-acid water solution of about 1 mol/l or the sodium-hydroxide water solution of about 1 mol/l was dropped, and pH was united with 8.0**0.5. Next, it washed using ion exchange water after filtering the generated precipitation until nitrate ion was no longer detected by the penetrant remover. After drying the obtained cake at 120 degrees C for 24 hours, it calcinated at 350 degrees C among air further for 5 hours. Furthermore, this thing was classified in 20-40 meshes, and the target catalyst was acquired.
[0063] The presentation of the acquired catalyst was Fe2O3:Cr2O3:aluminum2O3=80:15:5 (weight ratio).
[0064] In the approach of the example 18 of a catalyst - the examples 15-17 of 20 catalysts, the catalyst was prepared by the same approach as examples 1-3 except using 55g (Zn(NO3) 2.6H2O) of zinc nitrate instead of a chromium nitrate.
[0065] The presentation of the acquired catalyst was Fe2O3:ZnO:aluminum2O3=80:15:5 (weight ratio).
[0066] The coil made from stainless steel with a [reaction approach] bore of 20mm was filled up with the above-mentioned catalyst of the specified quantity. Specified quantity supply was carried out and wood ether and a steam were made to react to this coil at predetermined temperature.
[0067] The gas chromatograph analyzed the resultant and unreacted object which were obtained by the above actuation.

[0068] A [reaction condition and experimental result] reaction condition and an experimental result are shown in tables 5 and 6.
[0069]
[A table 5]

第 5 表

			触媒例15	触媒例16	触媒例17
触媒（重量比）			Fe_2O_3-Cr_2O_3-Al_2O_3 (80 : 15 : 5)		
条件	温度 (℃)		300	350	400
	H_2O/ジメチルエーテル（モル比）		10	10	10
	空間速度 (h^{-1})		25000	25000	25000
反応成績	ジメチルエーテル転化率 (%)		93.7	100	100
	収率 (%)	水素	91.9	95.8	93.6
		メタノール	0.1	0.1	0.2
		炭化水素	0.2	0.9	1.9
		CO	1.5	3.2	4.3

[0070]
[A table 6]

第 6 表

			触媒例18	触媒例19	触媒例20
触媒（重量比）			Fe_2O_3-ZnO-Al_2O_3 (80 : 15 : 5)		
条件	温度 (℃)		300	350	400
	H_2O/ジメチルエーテル（モル比）		10	10	10
	空間速度 (h^{-1})		25000	25000	25000
反応成績	ジメチルエーテル転化率 (%)		89.1	100	100
	収率 (%)	水素	87.6	94.0	92.1
		メタノール	0.1	0.1	0.1
		炭化水素	0.1	1.3	1.1
		CO	1.3	4.6	6.7

[0071] The example 21 of a catalyst - 49.4g (Co(NO3) 2.6H2O) of 28 cobaltous acetate were dissolved in about 300ml of ion exchange water, and evaporation to dryness of the 90g (the product made from the JGC chemistry, N612) of the gamma-alumina was further supplied and carried out to this water solution. And this thing was dried at 120 degrees C among air for 24 hours, and it calcinated at 500 degrees C among air further for 3 hours. Subsequently, among the hydrogen air current, processing was performed at 500 degrees C for 3 hours, and the catalyst was acquired.
[0072] The presentation of the acquired catalyst was Co:aluminum2O3=10:90 (weight ratio).
[0073] The coil made from stainless steel with a [reaction approach] bore of 20mm was filled up with the above-mentioned catalyst of the specified quantity. Specified quantity supply was carried out and wood ether, the steam, and/or the carbon dioxide were made to react to this coil at predetermined temperature.
[0074] The gas chroma graph analyzed the resultant and unreacted object which were obtained by the above actuation.
[0075] A [reaction condition and experimental result] reaction condition and an experimental result are shown in tables 7 and 8.
[0076]
[Equation 6]

$$CO_2\text{収率}(\%) = \frac{1/4 \times CO_2\text{生成速度}}{\text{ジメチルエーテル供給速度}} \times 100$$

The units of each rate are all. [mol/g-cat-h] [0077]
[A table 7]

第 7 表

			触媒例21	触媒例22	触媒例23	触媒例24
反応条件	温度 (℃)		250	300	350	400
	H_2O/ジメチルエーテル (モル比)		4	4	4	4
	CO_2/ジメチルエーテル (モル比)		0	0	0	0
	空間速度 (h^{-1})		8000	8000	8000	8000
反応成績	ジメチルエーテル転化率 (%)		93.8	100	100	100
	収率 (%)	合成ガス	84.6	91.8	92.0	88.8
		メタノール	0.3	0.3	0.5	0.9
		炭化水素	0.4	1.1	3.1	6.5
		CO_2	8.5	6.8	4.4	3.6
	合成ガス中 H_2／CO (モル比)		2.63	2.45	2.36	2.22

[0078]
[A table 8]

第 8 表

			触媒例25	触媒例26	触媒例27	触媒例28
反応条件	温度 (℃)		300	400	500	350
	H_2O/ジメチルエーテル (モル比)		0	0	0	2
	CO_2/ジメチルエーテル (モル比)		1	1	1	0.5
	空間速度 (h^{-1})		5000	5000	5000	5000
反応成績	ジメチルエーテル転化率 (%)		83.7	100	100	96.8
	収率 (%)	合成ガス	80.1	88.4	84.1	90.4
		メタノール	0	0	0	0.6
		炭化水素	3.6	8.9	15.9	2.5
		CO_2	—	—	—	3.3
	合成ガス中 H_2／CO (モル比)		0.96	0.88	0.61	1.53

[0079] Evaporation to dryness of the 100g (the product made from the Kanto chemistry, special grade chemical) of the zinc oxides was thrown in and carried out to the water solution made to dissolve the example 29 of a catalyst, 6ml of 30 hydrochloric acids, and 8.33g (PdCl2) of palladium chlorides in about 500ml of ion exchange water. It dried at 120 degrees C among air for 24 hours, and this was further calcinated at 500 degrees C among air for 3 hours. Subsequently, after having supplied this thing in the water solution which dissolved 10g of sodium hydroxides in about 1000ml of ion exchange water, heating it at 50 degrees C and performing processing of about 1 hour, it washed until the chloride ion was no longer detected, and dried at 120 degrees C for 24 hours. Furthermore, after carrying out the particle size regulation of this thing to 20-40 meshes by compression molding, among the hydrogen air current, processing was performed at 500 degrees C for 3 hours, and the catalyst was acquired.
[0080] The presentation of the acquired catalyst was Pd:ZnO=5:100 (weight ratio).

[0081] In the approach of the example 31 of a catalyst, and the examples 29 and 30 of 32 catalysts, the catalyst was prepared by the same approach as the examples 29 and 30 of a catalyst except using cerium oxide (the product made from the Kanto chemistry, special grade chemical) instead of a zinc oxide.
[0082] The presentation of the acquired catalyst was Pd:CeO 2= 5:100 (weight ratio).
[0083] After supplying and carrying out evaporation to dryness of the 100g (the product made from the JGC chemistry, N612) of the gamma-alumina to the water solution made to dissolve the example 33 of a catalyst, 6ml of 34 hydrochloric acids, and 8.33g (PdCl2) of palladium chlorides in about 500ml of ion exchange water, it dried at 120 degrees C among air for 24 hours, and calcinated at 500 degrees C among air further for 3 hours. Subsequently, without performing washing, after having supplied this thing in the water solution which dissolved 50g of sodium hydroxides in about 1000ml of ion exchange water, heating it at 50 degrees C and performing processing of about 1 hour, it dissociated and dried by the request. After carrying out the particle size regulation of this thing to 20-40 meshes by compression molding furthermore, among the hydrogen air current, processing was performed at 500 degrees C for 3 hours, and the catalyst was acquired.
[0084] The presentation of the acquired catalyst was Pd:Na2 O:aluminum2O3=5:0.4:100 (weight ratio).
[0085] Evaporation to dryness of the silica gel (Devi Fuji Son chemistry, ID) 100g was supplied and carried out to the water solution made to dissolve the example 35 of a catalyst, 6ml of 36 hydrochloric acids, and 8.33g (PdCl2) of palladium chlorides in about 500ml of ion exchange water. It dried at 120 degrees C among air for 24 hours, and this was further calcinated at 500 degrees C among air for 3 hours. Subsequently, washing and desiccation were performed, after having supplied this thing in the water solution which dissolved 10g of calcium hydroxides in about 1000ml of ion exchange water, heating at 50 degrees C and performing processing of about 1 hour. It dried, after supplying and carrying out evaporation to dryness of about 80g of this thing to the water solution which dissolved 6.6g of calcium hydroxides in about 200ml of ion exchange water furthermore. After carrying out the particle size regulation of this thing to 20-40 meshes by compression molding, among the hydrogen air current, processing was performed at 500 degrees C for 3 hours, and the catalyst was acquired.
[0086] The presentation of the acquired catalyst was Pd:CaO:SiO 2= 5:5:100 (weight ratio).
[0087] The coil made from stainless steel with a [reaction approach] bore of 20mm was filled up with the above-mentioned catalyst of the specified quantity. Specified quantity supply was carried out and wood ether, the steam, and/or the carbon dioxide were made to react to this coil at predetermined temperature.
[0088] The gas chromatograph analyzed the resultant and unreacted object which were obtained by the above actuation.

[0089] A [reaction condition and experimental result] reaction condition and an experimental result are shown in tables 9 and 10.
[0090]
[A table 9]

第 9 表

			触媒例29	触媒例30	触媒例31	触媒例32
触媒 (重量比)			Pd - ZnO (5 : 100)		Pd - CeO_2 (5 : 100)	
反応条件	温度 (℃)		300	350	300	350
	H_2O/ジメチルエーテル (モル比)		5	0	5	0
	CO_2/ジメチルエーテル (モル比)		0	1	0	1
	空間速度 (h^{-1})		12000	7000	12000	7000
反応成績	ジメチルエーテル転化率 (%)		99.7	89.4	91.4	90.2
	収率 (%)	合成ガス	93.6	87.2	83.4	87.6
		メタノール	0.2	0	0.3	0
		炭化水素	2.8	2.2	3.3	2.6
		CO_2	3.1	—	4.4	—
	合成ガス中 H_2/CO (モル比)		2.46	0.95	2.20	0.84

[0091]
[A table 10]

第 10 表

			触媒例33	触媒例34	触媒例35	触媒例36
触媒 (重量比)			$Pd-Na_2O-Al_2O_3$ (5 : 0.4 : 100)		$Pd-CaO-SiO_2$ (5 : 5 : 100)	
反応条件	温度 (℃)		300	350	300	350
	H_2O/ジメチルエーテル (モル比)		5	0	5	0
	CO_2/ジメチルエーテル (モル比)		0	1	0	1
	空間速度 (h^{-1})		12000	7000	12000	7000
反応成績	ジメチルエーテル転化率 (%)		88.9	84.9	95.1	73.8
	収率 (%)	合成ガス	79.5	83.7	86.1	72.1
		メタノール	0.1	0	0.1	0.1
		炭化水素	4.1	1.2	5.1	1.7
		CO_2	5.2	—	3.8	—
	合成ガス中 H_2/CO (モル比)		2.38	0.88	2.51	0.89

Hereafter, the example of this invention is explained based on a drawing. Drawing 1 is the schematic diagram showing an example of the generation-of-electrical-energy approach which uses the wood ether reformed gas of this invention.
[0092] By the sintering-machine cooler 1, air quenching of the sintered ore is carried out, and the 200-500-degree C exhaust gas which occurred on this occasion is sent to the heat exchanger 2 for the heat of hydration, the heat exchanger 3 for material gas heating, and the heat exchanger 4 for heat carrier heating. The heat carrier heated with the exhaust gas sensible heat of a sintering-machine cooler is sent to the wood ether refining reactor 5. With this equipment, the mixed gas which consists of the wood ether, steam, and carbon dioxide gas which it preheated with sintering-machine exhaust gas beforehand is introduced into two or more coils arranged inside a refining machine. The interior of a coil is filled up with the catalyst for wood ether refining, and when the mixed gas which changes from wood ether, steam, and carbon dioxide gas to this catalyst contacts, the mixed gas of a carbon monoxide and hydrogen generates. Although the internal temperature of a refining reactor changes with classes of catalyst with which it fills up, it is a 200-500-degree C temperature requirement in general. Into the generated reformed gas, the reformed gas with which wood ether itself is fuel gas which has calorific value with big little ** rare **, therefore unreacted wood ether contained wood ether does not have trouble in any way as a fuel of the combustor for gas turbines. The obtained reformed gas is sent to a combustor 6, and burns by the combustion air supplied from a compressor 7. The exhaust gas which occurs with a combustor is sent to a gas turbine 8, rotates a generator 9, and is generated. The gas discharged from a gas turbine is sent to the gas turbine exhaust-heat-recovery boiler 10. The steam obtained by the gas turbine exhaust-heat-recovery boiler is used as a process steam in an iron mill (not shown).
[0093] The generation-of-electrical-energy trial by the simple open sand mold gas turbine was carried out using the wood ether reformed gas obtained by the examples 1-4 of a generation of electrical energy, and the example of comparison generation of electrical energy predetermined example of a catalyst.
[0094]
[A table 11]

第 11 表

		発電例1	発電例2	発電例3	発電例4	比較発電例
条件	改質ガス	触媒例2	触媒例5	触媒例10	触媒例27	比較反応例
条件	改質ガス温度 (℃)	337	334	329	342	320
条件	排ガス温度 (℃)	570	561	547	584	530
結果	発電効率 (%)	44.6	44.3	43.6	45.8	41.5

[0095]
[A table 12]

第 12 表

			比較反応例
触媒 (重量比)			$CuO-ZnO-Al_2O_3$(30 : 20 : 50)
条件	温度 (℃)		360
条件	H_2O/メタノール (モル比)		2
条件	空間速度 (h^{-1})		15000
反応成績	メタノール転化率 (%)		84.2
反応成績	収率 (%)	水素	73.9
反応成績	収率 (%)	CO_2	21.5
反応成績	収率 (%)	CO	4.6

[0096]
[Effect of the Invention] As mentioned above, since according to this invention it constituted so that wood ether might be reformed using waste heat and the obtained reformed gas might be generated as a fuel for prime movers, the inside [of 200-500 degrees C] low-temperature waste heat discarded conventionally can use effectively, and since the carburation rate of the reformed gas moreover obtained is large, it has remarkable effectiveness -- the effectiveness of a generation of electrical energy improves.

[Translation done.]

DRAWINGS

[Drawing 1]

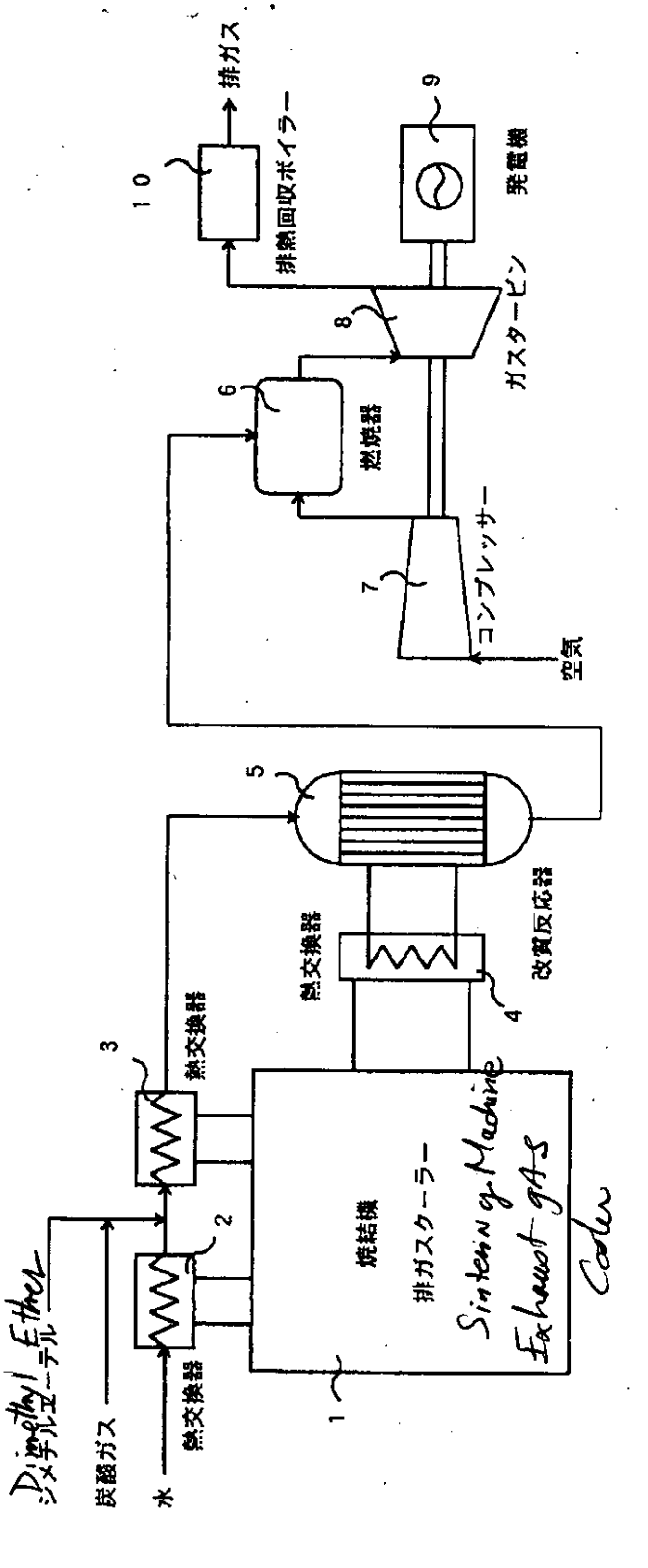

Fig. 4

[Translation done.]